Fe(II)-Na(I)-Ca(II) cation exchange on montmorillonite in chloride medium: Evidence for preferential clay adsorption of chloride - Metal ion pairs in seawater.

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Fe(II)-Na(I)-Ca(II) cation exchange on montmorillonite in chloride medium; evidence for preferential clay adsorption of chloride – metal ion pairs in seawater.

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Abstract

Fe(II)-Ca(II), Fe(II)-Na(I), and Fe(II)-Ca(II)-Na(I) exchange experiments on montmorillonite were performed in chloride background. These experiments show the possible sorption of Fe^{2+} and $FeCl^{+}$ ion pairs in exchange site positions, a result confirmed with 77 K ^{57}Fe Mössbauer experiments. The sorption data were modeled and the cation exchange selectivity for Fe(II) were found to be nearly equal to that of Ca(II). Vanselow selectivity coefficients, for Na-Fe^{2+} and Na-$FeCl^{+}$ reactions, were found to be equal to 0.4 (0.5 for Ca^{2+}) and 2.3 (2.5 for $CaCl^{+}$) respectively. High affinity of montmorillonite for chloride ion pairs seems to be a common mechanism as first stated by Sposito et al. (Sposito et al., 1983a), and should have implications *e.g.* on the chemistry of suspended particles in seawater. Exchange selectivity coefficients derived from this study and others were used to model experimental data on river water and seawater equilibrated particles. The agreement between simulations and experimental data is very good. The simulation shows the predominance of monovalent ion (Na^{+} and chloride ion pairs) sorption on clay particles in seawater. This sorption of monovalent ions leads to the dispersion of particles in seawater and to the extension of a "plume" of particles spreading away from river deltas, such as that of the River Amazon.

Keywords: cation exchange, ion pair, montmorillonite, clay, iron, seawater, river

1. Introduction

Aqueous ferrous iron is an important reductant in a variety of natural anoxic environments (eutrophic lakes, fjords and ocean trenches, ocean and swamp sediments, hydromorphic soils and anoxic groundwaters). The fate of this cation depends on its uptake – or sorption – at the surface of natural particles, such as organic matter, oxides and phyllosilicates. Sorption mechanisms vary from uptake by hydrophobic forces to uptake leading to the formation of covalent bonds. On phyllosilicate surfaces, according to chemical analyses and spectroscopic studies, cations are sorbed by two distinct mechanisms: cation exchange in the interlayer planes of the clay particles, and specific sorption at the edges of the platelets (e.g. Fletcher and Sposito, 1989; Charlet et al., 1993; Zachara and Smith, 1994; Bradbury and Baeyens, 1997; Bradbury and Baeyens, 1999; Schlegel et al., 2001; Bradbury and Baeyens, 2002). The clay sorption capacity has been well established for a wide range of potential pollutants in Na^+ and Ca^{2+} background cationic media. However, the influence of background anionic media such as Cl(-I) is poorly documented and thermodynamic data on sorption of Fe(II) by cation exchange are very rare, although Fe(II) is a species which has a great importance in anoxic surface water.

Two decades ago, Sposito et al. (Sposito et al., 1983a; Sposito et al., 1983b) proposed that high chloride concentrations lead to the formation of divalent cations-chloride ion pairs in the interlayer of smectitic particles. Estimations of thermodynamics constants for calcium-chloride, magnesium-chloride and strontium-chloride ion pairs were given in Fletcher and Sposito (Fletcher and Sposito, 1989). The relevance of this cation – anion – clay interaction model was tested by various exchange experiments (e.g. Suarez and Zahow, 1989; Rhue and Reve, 1990; Zhang and Sparks, 1996), producing conflicting data and various conceptual models. Despite a detailed analysis of the source of apparent conflicts between these data (Sposito, 1991), owing principally to experimental conditions such as clay content, divalent cation – chloride ion pairs are not usually considered in thermodynamics exchange calculations. For instance, they are not considered in the exchange

databases provided with PHREEQC2 (http://www.geo.vu.nl/users/posv/phreeqc.html). More recently, the presence of $CdCl^+$ ion pairs was detected in exchange position thanks to NMR study (Di Leo and O' Brien, 1999). Evidences of the presence of $CaCl^+$ ion pairs in the interlayer of Swy-1 montmorillonite particles equilibrated with 1 M $CaCl_2$ were also identified by X-ray diffraction and near infrared diffuse reflectance experiments (Ferrage et al., Submitted). Owing to the great selectivity coefficient of divalent cation – chloride ion pairs for exchange position in clay interlayer (Fletcher and Sposito, 1989), they should have a great impact on the clay exchanger composition in high chloride concentration background such as marine environment.

The present study aims to investigate the Fe(II) sorption in cation exchange site positions in chloride medium. The results are discussed in terms of Ca(II), Mg(II) and Fe(II) distribution in chloride rich media, and the change of distribution patterns as a function of chloride concentration, *e.g.* as particles move through an estuary.

2. Materials and Methods

2.1. Chemicals

All solutions and suspensions were prepared in a laboratory glove box with boiled, argon-degassed Millipore Milli-Q 18 MΩ water. NaOH and HCl stock solutions were made from Titrisol ampoules. $FeCl_2$, NaCl, and $CaCl_2$ solutions were prepared from analytical grade salts.

2.2. Clay material preparation and characterization

MX80 natural clay sample material (commercial Wyoming bentonite, reference BF100, CETCO France) was obtained from ANDRA (the French National Radioactive Waste Management Agency) after undergoing a homogenization treatment by quartering (Sauzéat et al., 2001). The

sample was dispersed in deionized water and the fine fraction (< 2 μm) isolated by sedimentation. After saturating the suspension with NaCl (0.5 M), it was successively treated with a 0.1 M acetic acid, 0.5 M NaCl solution to remove carbonates, then with a dithionate-citrate-bicarbonate solution (DCB + 0.5 M NaCl), and finally with 3% H_2O_2, 0.5 M NaCl to remove mineral impurities and organic matter (Schlegel, 2000). The final suspensions were washed with either 0.5 M NaCl or 0.05 M $CaCl_2$ solutions and then degassed with argon.

The fine fraction of the MX80 montmorillonite has the following structural formula (Tournassat et al., 2004b):

$(Si_{3.98}Al_{0.02})(Al_{1.61}Fe^{3+}_{0.13}Fe^{2+}_{0.02}Mg_{0.24})O_{10}(OH)_2Na_{0.28}$ for the Na-saturated form and $(Si_{3.98}Al_{0.02})(Al_{1.61}Fe^{3+}_{0.13}Fe^{2+}_{0.02}Mg_{0.24})O_{10}(OH)_2Ca_{0.14}$ for the Ca-saturated form.

Its cation exchange capacity corresponds to its structural charge, i.e. is equal to about 0.76 eq kg^{-1}.

2.3. Fe(II) – Na(I), Fe(II) – Ca(II) and Fe(II) – Ca(II) – Na(I) Exchange experiments

Tournassat and Charlet have shown that Fe(II) sorbs specifically onto clay minerals above pH 3.5 (Tournassat, 2003; Tournassat et al., Submitted). Hence, to avoid specific sorption of Fe(II), the following exchange experiments were conducted at low pH (pH value between 2.1 and 3.6, depending on the experiment). At this pH, dissolution of montmorillonite is likely to occur. However, the kinetics of dissolution is too slow to affect significantly the cation exchange reaction by decreasing the amount of available exchange sites or by producing competing cations such as Mg^{2+} (Tournassat, 2003; Tournassat et al., Submitted).

We used the experimental procedure designed by Sposito et al. for exchange experiments (Sposito et al., 1981; Sposito et al., 1983a; Sposito et al., 1983b). All experiments were conducted in a N_2/H_2 atmosphere glove box (Coy Laboratory Products Inc.) in which the pO_2 was monitored continuously by a Jacomex O_2 sensor. The O_2 content never exceeded 10 ppm in the glove box atmosphere. Centrifugation tubes were numbered and precisely weighed (m_{tube} in g) with a Mettler

Toledo AG285 balance. All volumes were added with a calibrated micropipette. A known volume of clay suspension was added to each 17-ml centrifuge tube (V_{susp}, clay content ρ). Adequate volumes of acidified NaCl, $CaCl_2$ and $FeCl_2$ were then added (V_{NaCl}, V_{CaCl_2} and V_{FeCl_2}, concentrations C_{NaCl}, C_{CaCl_2} and C_{FeCl_2}). In each experiment, the concentrations of NaCl, $CaCl_2$ and $FeCl_2$ solutions were chosen to obtain a constant total normality of the final suspension. Total normalities and clay contents are shown in table I for each experiment. The tubes were shaken for one week, then centrifuged and the supernatant filtered out. The pH was measured with a microelectrode (Mettler Toledo, Inlab 423). An aliquot of supernatant was filtrated and diluted for Na, Ca and Fe measurement. Na and Ca were measured on a Perkin-Elmer Optima 3300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Fe(II) was measured in the glove box on a Hach DR/2010 spectrophotometer using the O-phenantrolin method (Rodier, 1996). The centrifuged reaction tubes, containing the clay slurry, were weighed ($m_{centrif}$) and 10 ml of 1 M ammonium acetate were added to each tube. They were shaken for one week. The supernatant was then filtrated and diluted, and the concentrations of Na and Ca were measured (C_{Amm}^{Na} and C_{Amm}^{Ca} respectively) by ICP-AES. Exchanged Na(I) and Ca(II) in eq kg^{-1} were then calculated according to:

$$q_{Na} = \frac{C_{Amm}^{Na} \times 10 \times d - C_{sol}^{Na} \times \left(m_{centrif} - m_{tube} - \left(V_{susp} \times \rho \times d\right)\right)}{\left(V_{susp} \times \rho\right)} \qquad \text{in eq kg}^{-1} \qquad [1]$$

$$q_{Ca} = 2 \times \frac{C_{Amm}^{Ca} \times 10 \times d - C_{sol}^{Ca} \times \left(m_{centrif} - m_{tube} - \left(V_{susp} \times \rho \times d\right)\right)}{\left(V_{susp} \times \rho\right)} \qquad \text{in eq kg}^{-1} \qquad [2]$$

where volumes are given in ml, concentrations in mol l^{-1}, clay contents in g l^{-1} and masses in g. The density d of all solutions is taken equal to 1.0. The exchanged Fe(II) (q_{Fe}) was determined by subtracting the Fe(II) measured in the supernatant (C_{meas}^{Fe}) from the total Fe(II) added to the tube (C_{added}^{Fe}):

$$q_{Fe} = 2 \times \frac{C_{added}^{Fe} - C_{meas}^{Fe}}{\left(V_{susp} \times \rho\right)} \quad \text{in eq kg}^{-1} \quad [3]$$

The total Fe(II) corresponds to the Fe(II) added concentration plus the Fe(II) originating from the dissolution of the clay material. This value was approximated using dissolution experiments conducted at low pH and high Ca concentration in order to avoid re-adsorption of dissolved Fe(II) in exchange site positions. The error bands were calculated using a 2% standard error on the concentration measurements for Na and Ca and 3% for Fe(II).

2.4. MÖSSBAUER EXPERIMENTS

The preparation of the Mössbauer samples was conducted in a more efficient glove box than that previously used for the exchange experiments, *i.e.* a Jacomex N_2 atmosphere glove box in which the pO_2 was monitored continuously by a Jacomex O_2 sensor. For this experiment, the O_2 content never exceeded 1 ppm in the glove box atmosphere. 100 mg of $^{57}Fe(0)$ were dissolved in concentrated HCl (0.1 mol l^{-1}) at ~100 °C. Then, the dissolved iron was put in the glove box and diluted in deionized water to a final volume of 100 ml, to obtain a ~1000 ppm $^{57}Fe(II)$ stock solution. The acidic conditions prevented the oxidation of the suspension prior to its transfer to the glove box. Several cycles of centrifugation and washing with deionized water were conducted to decrease the NaCl concentration in the Na-conditioned clay stock suspension outside of the glove box. This washing of the clay facilitates the sorption of Fe(II) in cation exchange site positions by a mass action phenomenon: the less Na^+ in solution, the less competitive is Na^+ for exchange site positions. This new Na-conditioned clay stock suspension was degassed with a stream of N_2 for one night, put in the glove box and allowed to equilibrate with the free O_2 atmosphere for one day. Then, the suspension and the $^{57}Fe(II)$ stock solution were mixed to obtain a $^{57}Fe(II)$ exchanged clay. After three days reaction time, the sample was centrifuged, the supernatant was removed and the clay slurry was transferred to spectrometer sample holders that had been preequilibrated for one

week in the glovebox. These sealed holders were then taken out of the glovebox and immediately frozen before being transported to the Mössbauer facility. The Mössbauer spectrum of the Na-conditioned smectite was recorded at 77 K using a constant acceleration spectrometer and a ^{57}Co source diffused into a rhodium matrix. Velocity calibrations were made using α-Fe foil at 300 K. The hyperfine parameters were refined using a least-squared fitting procedure (unpublished MOSFIT program, Teillet and Varret, University of Maine, Le Mans, France).

2.5. FLOCCULATION EXPERIMENTS

Clay suspensions in 0.05 M and 0.5 M calcium chloride and calcium perchlorate media were prepared using the clay stock suspension. The clay suspensions were then further diluted in 0.05 M and 0.5 M calcium chloride and calcium perchlorate solutions in order to obtain 0.6 g l^{-1} clay suspensions. These suspensions were put in special glass cells for spectrophotometric analyses (Merck 1.14725.0001). After vigorous shaking (Minishaker IKA MS1) and ultrasonication (3 min), the suspensions were allowed to flocculate. In one experiment, the kinetics of the flocculation was observed by photographing the tubes as a function of time (10 ml suspension in each tube). In the other experiment, the absorbency (5 ml suspension in each tube) was measured as a function of time in a portable data-logging spectrophotometer (Hach DR/2010) at 400 or 650 nm wavelength (Schramm and Kwak, 1982).

3. Results of exchange experiments

In many cation exchange studies (e.g. Sposito, 1981; McBride, 1994), the equivalent fraction of one cation in solution ($\widetilde{E}_{Cat}$, where Cat is a cation species) is plotted as a function of the equivalent fraction of the cation on the exchanger phase (E_{Cat}). For Fe(II) in a Na(I) – Ca(II) – Fe(II) system, these equivalent fractions are calculated according to the following formulas:

$$\widetilde{E}_{Fe} = \frac{2 \times [Fe(II)]}{2 \times [Fe(II)] + 2 \times [Ca(II)] + [Na(I)]} \quad [3]$$

$$E_{Fe} = \frac{q_{Fe}}{q_{Fe} + q_{Ca} + q_{Na}} \quad [4]$$

where [*Fe(II)*], [*Ca(II)*] and [*Na(I)*] are the solution concentrations of Fe(II), Ca(II) and Na(I) (in mol l^{-1}) respectively. The method used to obtain q_{Fe} (Eq. 3) leads to a greater extent of the error band for q_{Fe} than for q_{Ca} and q_{Na} (Eq. 2). Hence, the error on the E_{Fe} is large, despite of the good precision on q_{Ca} and q_{Na} data. Plotting E_{Fe} as a function of $\widetilde{E}_{Fe}$ would have lead to a loss of much information because the information on q_{Fe}, q_{Ca} and q_{Na} are gathered. Thus, we decided to use q_i (in eq kg^{-1}), the amount of sorbed cation species *i* and to plot it as a function of the equivalent fraction of Fe(II) in solution ($\widetilde{E}_{Fe}$), in order to fully exploit q_{Ca} and q_{Na} data as well as q_{Fe} data. Figure 1 shows the results of the exchange experiments. As first stated by Sposito et al. (Sposito et al., 1983a; Sposito et al., 1983b) and re-demonstrated by Tournassat et al. (Tournassat et al., 2004a; Tournassat et al., 2004b), the sorbed amount of divalent cationic species on a clay exchanger in Cl^- anionic background is a methodologically defined quantity, since ion pairs (e.g. $CaCl^+$) are also adsorbed in cation exchange positions. Thus, the apparent CEC (Cation Exchange Capacity), which is equal to the sum of all q_i, varies from one experiment to another (figure 1). For example, q_{Ca} in the first point of experiment A (*i.e.* in the case of a pure Ca–exchanged clay) is greater than q_{Na} in the first point of experiment C (*i.e.* in the case of a pure Na-exchanged clay). This difference is attributed to the sorption of $CaCl^+$ ion pairs, which are taken into account twice in equation 2 (Sposito et al., 1983a; Sposito et al., 1983b; Tournassat et al., 2004b). If $FeCl^+$ sorbed like $CaCl^+$ on the clay exchanger phase, then one would expect the apparent CEC to increase as a function of $\widetilde{E}_{Fe}$ in the Na(I)-Fe(II) exchange experiment. The trend of the results shown on figure 1 confirms this point but the error bands associated with q_{Fe} are too large to unambiguously prove the sorption of $FeCl^+$. Nevertheless, Fe(II) and Ca(II) seem to have the same overall behavior towards the clay

exchanger phase. To further confirm this point, the non-preference isotherm of Fe(II) – Ca(II) exchange was compared to the Fe(II) – Ca(II) data (figure 2). Clearly, as the non-preference isotherm perfectly fits the data, we can conclude that $FeCl^+$ sorbs on the clay exchanger phase exactly in the same way as $CaCl^+$.

4. Modeling cation exchange data

The Vanselow Convention (Vanselow, 1932; Sposito, 1981) was used to model the data. In this convention, the activity of a surface species is taken equal to its mole fraction within the exchanger phase. The PHREEQC2 code (Parkhurst and Appelo, 1999) is used as a versatile computer code amenable to handling the various models used to describe cation exchange and surface complexation. The Llnl.dat database is used for the calculation of speciation in solution together with the structural CEC of the MX80 montmorillonite and the cation exchange selectivity coefficients for H^+, Na^+, Ca^{2+} and $CaCl^+$, obtained from Tournassat et al. (Tournassat et al., 2004a), allowing only two parameters to be refined: the cation exchange selectivity coefficients for Fe^{2+} and $FeCl^+$ respectively. The refined values are shown in table II. We need to slightly adjust the previously obtained Ca^{2+} exchange selectivity coefficient to obtain a better fit of the data, but this adjustment lies in the error band of the published coefficients (Tournassat et al., 2004a). Figure 1 shows the closeness of the fit. According to the closeness of fit reported in figure 1, one has to emphasize that binary systems – Na(I)-Fe(II) or Ca(II)-Fe(II) –, as well as ternary systems – Na(I)-Ca(II)-Fe(II) – are adequately described within the limits of the error bands. It was not possible to obtain a reasonable fit of the data without introducing a cation exchange selectivity coefficient for $FeCl^+$. Fe^{2+} and Ca^{2+} have similar exchange selectivity coefficients (log K_v = 0.4 and 0.5, respectively, with respect to Na^+). $CaCl^+$ has a greater exchange selectivity coefficient than that of $FeCl^+$ (log K_v = 2.5 and 2.3 with respect to Na^+, respectively), but the association constant of the reaction:

$Ca^{2+} + Cl^- \Leftrightarrow CaCl^+$ $\log K_a = -0.696$ Reaction 1

is lower than the association constant of the reaction (Llnl.dat database, given with the PHREEQC2 new version):

$Fe^{2+} + Cl^- \Leftrightarrow FeCl^+$ $\log K_a = -0.167$ Reaction 2

Thus, $CaCl^+$ is slightly preferred over $FeCl^+$ on the exchanger phase, but $FeCl^+$ forms in greater amounts than $CaCl^+$, at equal total solution normality. Consequently, the two ion pairs are sorbed in comparable amounts and, as a result, the clay exchanger appears not to have any preference for Fe(II) or Ca(II). Indeed figure 1A looks the same as figure 2. Sposito et al. (Sposito et al., 1983a) had further demonstrated the high affinity of clay surface for $MgCl^+$ ion pairs, Ca(II) and Mg(II) behaving similarly towards exchange on clay in chloride ionic background. Their experimental Mg(II)-Na(I) exchange data in perchlorate and chloride ion media were here applied (figure 3), together with Ca(II)-K(I) exchange data from Jensen (Jensen, 1973), using the same procedure as described above (figure 4). The results (table II) indicate that:

(i) the Mg^{2+} - Na^+ and Ca^{2+} - Na^+ exchange reactions have close cation exchange selectivity coefficients ($\log K_v = 0.4$ and 0.5, respectively);

(ii) the $MgCl^+$ - Na^+ exchange selectivity coefficient ($\log K_v = 1.9$) corresponds to the ratio between the association reaction constants for $CaCl^+$ ($\log K_a = -0.696$) and $MgCl^+$ ($\log K_a = -0.135$) ion pairs formation multiplied by the $CaCl^+$ - Na^+ exchange selectivity coefficient ($\log K_v = 2.5$). Then, at equal total solution normality, $MgCl^+$ and $CaCl^+$ have the same apparent affinity for clay exchange sites;

(iii) the $MgCl^+$ - Na^+, $CaCl^+$ - Na^+, and $FeCl^+$ - Na^+ exchange selectivity coefficients are significantly higher than the K^+-Na^+ and H^+-Na^+ exchange selectivity coefficients.

5. results of Mössbauer experiments

Mössbauer results are shown in figure 5, and the associated hyperfine parameters are shown in table III. The model that fits, for both frozen ^{57}Fe stock solution and ^{57}Fe exchanged clay, consists in two main quadrupolar doublets (A and B) attributed to two different Fe(II) surface species. The quadrupolar doublet due to the presence of Fe(III) in MX80 clay octahedral layer (Tournassat et al., 2004b) is almost undetectable. Other models that fit may be proposed, e.g. with additional quadrupolar components to be attributed to iron species with other environments. However, the presence of two Fe(II) Mössbauer components was a minimum to adjust the spectra. Since the presence of two Fe(II) components in the frozen ^{57}Fe stock solution Mössbauer spectrum is in good agreement with the Fe(II) solution chemistry (presence of Fe^{2+} and $FeCl^{+}$), the presence of two components (at least) in the $^{57}Fe(II)$ exchanged clay Mössbauer spectrum is in agreement with the presence of Fe^{2+} and $FeCl^{+}$ in cation exchange site positions. Solution and exchange speciation computation, under experimental conditions, indicates that Fe^{2+} is the main iron species in the solution, whereas $FeCl^{+}$ is the main iron species in the Fe(II) exchanged clay. By considering that part of the Mössbauer contribution A could be attributed to $FeCl^{+}$ species, the increase in the extent of contribution A, in the Fe(II) exchanged clay sample, is in agreement with these computations. Furthermore, the differences in quadrupolar splitting values of mean Fe(II) contributions denote the effect of the clay structure on Fe(II) when present in cation exchange site positions.

6. results of flocculation experiments

Flocculation kinetics are expected to increase with increasing ionic strength, due to the double layer thickness contraction. No significant difference in flocculation kinetics was observed between the suspensions equilibrated with 0.05 M calcium perchlorate and 0.05 M calcium chloride, whereas the flocculation kinetics of the 0.5 M calcium chloride equilibrated suspension were the slowest (figure 6 and 7). Unlike chloride, perchlorate does not form ion pairs with calcium in solution

(Hester and Plane, 1964). Hence, the difference in kinetics could originate from the presence of ion pairs in exchange positions. At a 0.05 M $CaCl_2$ concentration, the $CaCl^+$ ion pairs do not dominate the ion exchange composition and thus have no effect on the flocculation kinetics. At 0.5 M $CaCl_2$ concentration, the $CaCl^+$ ion pairs do dominate the ion exchange composition. The critical coagulation concentration is two orders of magnitude higher for monovalent species than for divalent species (e.g. Sposito, 1984) and thus, the particles will tend not to flocculate, i.e. to remain monodispersed, if $CaCl^+$ dominates in exchange positions.

7. Discussion

Table II shows the high clay affinity for monovalent chloride-bivalent cation ion pairs compared to monovalent cations like Na^+. This high clay affinity for chloride-bivalent cation ion pairs should have important implications in the modifications in exchanger composition of river suspended particles as the particles enter the ocean. In the following, this change has been modeled on the basis of the cation exchange selectivity coefficients given in table II.

Sayles and Mangelsdorf's study on Amazon River particles (Sayles and Mangelsdorf, 1979) was taken as a reference experimental study, as the Amazon River carries a large amount of clay particles. The clay fraction of Amazon River suspended matter consists mainly of kaolinite and montmorillonite. Quantitatively, the concentration of suspended montmorillonite exceeds by far the concentration of kaolinite in the Amazon River (Irion, 1983). Indeed the < 2 μm fraction of Amazon River suspended particles represents, at least, 54 % of the total particulate CEC and the CEC is mainly determined by montmorillonite due to its high CEC value (Sayles and Mangelsdorf, 1979). Sayles and Mangelsdorf measured the particle exchange composition in the Amazon River, together with the cation composition of the river water. Afterwards, they equilibrated their particles with seawater and analyzed the composition of the exchange species. Since no data on anionic composition in river water is given, concentrations of HCO_3^- and Cl^- were chosen so that (i) [HCO_3^-

] + [Cl^-] is equal to the total equivalent concentration of cations in solution and (ii) [Cl^-] is equal to 0.13 mmol l^{-1}, the mean Cl^- concentration in South American river water (Holland, 1978). We considered a simplified composition of the ocean, shown in table IV, to calculate the clay exchanger composition in seawater.

Figures 8 and 9 show the good agreement between the experimental and modeled equivalent sorbed fraction (X_{Me}) on the particles in equilibrium within the Amazon River for Ca and Mg species, which represent more than 95% of the exchanger composition. Therefore, a model based on montmorillonite surface chemistry is able to simulate the suspended particle exchange composition although the < 2 μm fraction of these particles represents only 54 % of the total CEC. The documented presence of kaolinite and illite (Irion, 1983; Martinelli et al., 1993), participating in the exchange capacity may account for the underestimation of K^+ sorption (figure 9). The poor agreement between experimental and modeled equivalent sorbed fraction of Na^+ is likely due to the low amount of sorbed Na^+ and hence to a supposed greater uncertainty on the value of q_{Na} data than on q_{Ca} and q_{Mg} data. By analyzing more precisely the results of the simulation, we note that the major cations of particle exchange composition are Ca^{2+} and Mg^{2+}. $CaCl^+$ and $MgCl^+$ are not sorbed in any significant amount on these particles, since the river water is a dilute system ($I_{mean} \approx 0.6$ mmol l^{-1}) and since Cl^- is not the predominant anion.

Sayles and Mangelsdorf (Sayles and Mangelsdorf, 1979) have further equilibrated their particles with seawater and analyzed the changes in particle exchange composition. As already stated, their experimental measurement method leads to an apparent overestimation of the metal equivalent fraction, as they took the amount of $CaCl^+$ and $MgCl^+$ sorbed onto the solid into account twice. The mean values for Na(I), Mg(II), Ca(II), and K(I) experimental sorbed equivalent fractions are shown in table V, for particles equilibrated with seawater, together with the equivalent fractions calculated with the exchange selectivity coefficients for montmorillonite, taking into account *free* species cation exchange equilibria listed in table II. As shown in the third column of table V, Amazon particles suspended in seawater show an exchange composition at variance with that

predicted, based on cation exchange of free species only, *i.e.* not taking into account ion pairs. On the contrary, the simulation including ion pair adsorption, while underestimating the sorbed K(I) fraction, and slightly overestimating the Mg(II) sorbed fraction, altogether gives a much better agreement with the experimentally measured particle exchange composition. The difference between the simulated and the experimental results for K^+ is attributed to the documented presence of illite or kaolinite (Irion, 1983; Martinelli et al., 1993) whose K^+ exchange selectivity coefficient is greater than that of montmorillonite particles (Jensen, 1973). The activity coefficient of ion species can also lead to some inaccuracy, since one may only use, with PHREEQC2, the Davies or Debye-Hückel activity coefficient relations, which are not appropriate models for seawater systems. However, in general, the whole tendency of sorption is respected and the sorption of ion pairs ($CaCl^+$ and $MgCl^+$) is obviously taking place in the marine environment, due to high Ca(II), Mg(II) and Cl(-I) concentrations.

Due to the presence of $MgCl^+$ and $CaCl^+$ in exchange position, the apparent CEC of clayey particles, based on the sum of equivalent cation concentrations in the clay exchanger (excluding H^+), should be higher when equilibrated with seawater, than when equilibrated with riverwater. The analysis of Sayles and Mangelsdorf data (Sayles and Mangelsdorf, 1979) shows that the apparent CEC of particles in seawater is 18 ± 6 % higher than in riverwater. Our model predicts an increase of 44 %. This difference is likely due to a possible overestimation of the $MgCl^+$ selectivity coefficient for samples being different than a pure montmorillonite. Decreasing the $MgCl^+$ selectivity coefficient to the value $\log K^{Na/MgCl} = 1.5$, the model predicts an apparent CEC increase of approximately 25 % in agreement with the observed one, and the following apparent exchangeable cation composition: Na 42 %, Mg 38 %, Ca 16 % and K 4 %, in full agreement with the measured one. Nevertheless, one other study shows no increase of the apparent CEC during particles transfer from riverwater to seawater, whereas changes in exchangeable cation composition are similar to those described previously (e.g. Sayles and Mangelsdorf, 1977). We should admit that this point is problematic.

Von Breymann and Suess (von Breymann and Suess, 1988) study on Mg-NH_4 exchange of clay particles equilibrated in seawater showed that approximately 40 % of the exchangeable cation composition of a nontronite (a smectite with tetrahedral charges) is due to the Mg contribution. This result, based on ^{27}Mg isotopic measurement is in agreement with Sayles and Mangelsdorf's results and with the results of our model. If no $MgCl^+$ is considered in the exchangeable cations composition, an unrealistic selectivity coefficient value should be applied to Mg^{2+} (log $K^{Na/Mg}$ = 1.2). By considering the presence of ion pairs in exchange position, it is possible to model their NH_4-Mg exchange results at low NH_4^+ content. Their nontronite sample has an apparent CEC value of 0.842 eq/kg. This value was measured thanks to the clay equilibration with a 0.5 N $MgCl_2$ solution, spiked with ^{27}Mg. In these experimental conditions, $MgCl^+$ should be present in the interlayer. Thus, the measured CEC should be greater than the structural one. By considering a log $K^{Na/MgCl}$ selectivity coefficient value of 1.5, the structural CEC value is calculated to be equal to 0.65 eq/kg and the apparent Mg concentration in exchange position is 0.32 eq/kg, to be compared with the measured value of 0.352 eq/kg . The selectivity coefficient value for NH_4^+ (log $K^{Na/NH4}$ = 0.7) is set to a value slightly higher than the selectivity coefficient for K^+, in agreement with previous studies (e.g. Fletcher and Sposito, 1989). The simulation results of von Breymann and Suess' Mg-NH_4 exchange experiment (von Breymann and Suess, 1988) is shown on figure 10. This experiment at low NH_4 concentration is successfully simulated. Nevertheless our model fails in simulating their experiment at high NH_4Cl concentration (0.15 M to 3 M, data not shown). This problem is likely due to the use of Debye-Hückel convention for activity coefficient calculation at high ionic strength.

8. Conclusion

As particles move into the estuary, their surface becomes increasingly saturated with $MgCl^+$, Na^+, and $CaCl^+$ species, i.e. with monovalent species. The critical coagulation concentration for these monovalent species is two orders of magnitude higher than for divalent species (see Sposito,

1984) and thus, the particles will tend not to flocculate, and to remain monodispersed. This tendency runs contrary to what could be expected, as a double layer thickness contraction is observed when ionic strength increases. This effect is clearly demonstrated by the flocculation experiments presented in figures 6 and 7. The clay suspension that has been equilibrated with a concentrated calcium chloride solution (0.5 M $CaCl_2$) flocculates less rapidly than the clay equilibrated with a 0.5 M calcium perchlorate solution or with a 0.05 M calcium chloride or perchlorate solution. Hence, the high chloride concentration in seawater and the subsequent presence of ion pairs in exchange positions reduces the rate of particle sedimentation when river water mixes with seawater and one observes the formation of a large plume of particles several hundred kilometers away from the Amazon River delta, along the Guyana coast.

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Table I. Cation exchange experimental conditions

	Experiment A	Experiment B	Experiment C	Experiment D	Experiment E	Experiment F
pH	3.37 ± 0.05	3.23 ± 0.02	2.17 ± 0.03	2.22 ± 0.09	3.59 ± 0.10	3.40 ± 0.08
Clay content ($g\ l^{-1}$)	5.85	3.90	8.25	8.25 and 5.50 *	5.85	3.90
Cations	Ca(II) – Fe(II)	Ca(II) – Fe(II)	Na(I) – Fe(II)	Na(I) – Fe(II)	Na(I) – Ca(II) – Fe(II)	Na(I) – Ca(II) – Fe(II)
Total Normality (T.N.) ($meq\ l^{-1}$) = [Cl^-]	49 ± 1	49 ± 3	132 ± 3	127 ± 8	50 ± 3 †	50 ± 3 ‡

* 8.25 $g\ l^{-1}$ for the first four experimental points and 5.50 $g\ l^{-1}$ for the other experimental points

† [Ca(II)] = 13.1 $mmol\ l^{-1}$ ± 0.5

‡ [Ca(II)] = 9.1 $mmol\ l^{-1}$ ± 0.3

Table II. List of cation exchange reactions and selectivity coefficients (Vanselow convention) for the Fe(II) – Na(I) – Ca(II) exchange experiments of this study, and for Na(I) – Mg(II) and K(I) – Ca(II) exchange experiments of published studies.

Exchange reaction	log K_v	Reference
$\equiv XNa + H^+ \Leftrightarrow \equiv XH + Na^+$	0.0	Fletcher and Sposito, 1989; Tournassat et al., 2004a
$\equiv XNa + K^+ \Leftrightarrow \equiv XK + Na^+$	0.6	This study (data from Jensen, 1973)
$\equiv XNa + CaCl^+ \Leftrightarrow \equiv XCaCl + Na^+$	2.5	Fletcher and Sposito, 1989; Tournassat et al., 2004a
$\equiv XNa + MgCl^+ \Leftrightarrow \equiv XMgCl + Na^+$	1.9	This study (data from Sposito et al., 1983a)
$\equiv XNa + FeCl^+ \Leftrightarrow \equiv XFeCl + Na^+$	2.3	This study
$2 \equiv XNa + Ca^{2+} \Leftrightarrow \equiv X_2Ca + 2\ Na^+$	0.5	Fletcher and Sposito, 1989; Tournassat et al., 2004a
$2 \equiv XNa + Fe^{2+} \Leftrightarrow \equiv X_2Fe + 2\ Na^+$	0.4	This study
$2 \equiv XNa + Mg^{2+} \Leftrightarrow \equiv X_2Mg + 2\ Na^+$	0.4	This study (data from Sposito et al., 1983a)

Table III. Mössbauer parameters of the ^{57}Fe-exchanged smectite and of the HCl acidified ^{57}Fe frozen solution. Error bands are indicated in brackets.

		I.S. mm s^{-1}	Γ mm s^{-1}	Q.S. mm s^{-1}	%
Frozen ^{57}Fe stock solution	Fe(II) A	1.37 (0.01)	0.29 (0.04)	3.37 (0.05)	40 (5)
	Fe(II) B	1.36 (0.01)	0.47 (0.04)	3.02 (0.05)	60 (5)
	Mean A+B	1.36 (0.02)		3.13 (0.05)	100
^{57}Fe exchanged clay	Fe(II) A	1.38 (0.01)	0.30 (0.04)	3.43 (0.05)	63 (5)
	Fe(II) B	1.40 (0.01)	0.49 (0.04)	3.10 (0.05)	37 (5)
	Mean A+B	1.39 (0.02)		3.31 (0.05)	100

I.S. = Isomer shift value quoted to that of α-Fe at 300 K; Γ = linewidth; Q.S. = quadrupolar splitting value; % = ratio of each component.

Table IV. Simplified composition of ocean water. Salinity = 36 ‰ (after Holland, 1978).

Ions	Concentrations (mmol kg^{-1})
Sodium	481
Magnesium	55
Calcium	11
Potassium	11
Chloride	564
Sulfate	29
Bicarbonate	2

Table V. Comparison of measured and simulated equivalent fraction of main cations sorbed on Amazon River suspended particles equilibrated with seawater. Simulation parameters are given in table II.

	Sorbed equivalent fraction (%)		
Cation	Experimental data †	Model without ion pairs	model with ion pairs
Na(I)	40 % ± 10 %	72 %	29 %
Mg(II)	40 % ± 10 %	18 %	57 %
Ca(II)	15 % ± 3 %	4 %	11.5 %
K(I)	8 % ± 1 %	6 %	2.5 %

† Sayles and Mangelsdorf, 1979.

Figure Captions

Figure 1. Fe(II) – Na(I) and Fe(II) – Ca(II) exchange data plotted as equivalent sorbed amount of ion i (q_i, eq kg^{-1}) as a function of the equivalent fraction of solute Fe(II), together with simulations whose parameters are given in table II. Experimental conditions are given in table I.

Figure 2. Comparison of Fe(II) – Ca(II) exchange data with a non-preference isotherm (see text for details).

Figure 3. Mg(II) – Na(I) exchange isotherm. Experimental data are from Sposito et al. (Sposito et al., 1983a). Model curves were computed with the parameters given in table II. Top: experiment in ClO_4^- anionic background medium. Bottom: experiment in Cl^- anionic background medium

Figure 4. Ca(II) – K(I) exchange isotherm dependence on the ionic strength in chloride medium. Data are from Jensen (Jensen, 1973) and simulated curves were computed with the selectivity coefficients given in table II. The data are plotted as apparent equivalent sorbed amounts (q_i where i denotes K^+, circles, or Ca(II), diamonds) as a function of equivalent K^+ fraction in solution. Ionic strength: I = 0.005 mol l^{-1} (top), and 0.05 mol l^{-1} (bottom). Error bands were not available from the referenced publication.

Figure 5. Dots: 77 K Mössbauer spectrum of ^{57}Fe exchanged clay (top) and frozen ^{57}Fe stock solution (bottom). Thin lines: sum of all the contributions of the decomposition. The parameters of the decomposition are given in table III. Contributions of Fe(II) A and Fe(II) B are combined. Arrows indicate the contribution of Fe(III).

Figure 6. Photos of the kinetics of 0.6 g l^{-1} clay suspension flocculation. Time in minutes is indicated on the figure together with the equilibrating ionic media. Note that the 0.5 M calcium chloride equilibrated suspension flocculates less rapidly than the suspensions equilibrated with a less concentrated ionic medium.

Figure 7. Kinetics of 0.6 g l^{-1} clay suspension flocculation observed by absorbency measurements. Top: 650 nm wavelength. Bottom: 400 nm wavelength. Open symbols: calcium perchlorate medium. Filled symbols: calcium chloride medium. Squares: suspensions equilibrated with 0.5 M Ca solutions. Triangles: suspensions equilibrated with 0.05 M Ca solutions. Note that the 0.5 M calcium chloride equilibrated suspension flocculates less rapidly than the suspensions equilibrated with a less concentrated ionic medium.

Figure 8. Cation exchange composition of particles suspended in the Amazon River. Comparison between experimental (Sayles and Mangelsdorf, 1979) and modeled apparent sorbed equivalent fractions (X_{Me}) of Na(I) (triangles), K(I) (circles), Mg (II) (squares) and Ca(II) (diamonds). The straight line depicts a 1:1 relationship, i.e. the perfect conformity of the model with the experimental points. Error bands were not available from the referenced publication.

Figure 9. Details of figure 8. Cation exchange composition of particles suspended in the Amazon River. Comparison between experimental (Sayles and Mangelsdorf, 1979) and modeled apparent sorbed equivalent fractions (X_{Me}) of Na(I) (triangles), K(I) (circles), Mg (II) (squares) and Ca(II) (diamonds). The straight line depicts a 1:1 relationship, i.e. the perfect conformity of the model with the experimental points. Error bands were not available from the referenced publication.

Figure 10. Mg desorption (open diamonds) and NH_4^+ sorption (closed squares) on nontronite as a function of NH_4 concentration in seawater. Experimental results from von Breymann and Suess

(von Breymann and Suess, 1988). The full line (Mg) and dashed line (NH_4^+) depicts the simulation of the results using the parameters given in table II and in the “discussion” section.